1st Semi-Annual Report on

NASA Grant NGR-05-020-066

from May 6, 1965 to November 6, 1965

PHOTOEMISSION STUDIES OF SOLIDS

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I. INTRODUCTION

The work presently supported by this NASA grant can be placed under
two general headings: 1) Fundamental studies of vacuum ultraviolet
photoemission, and 2) Development of the new experimental apparatus and
techniques necessary to facilitate this work.

It was possible to start both phases of this work before the NASA
support was granted because of temporary direct support granted by ARPA
through the Center for Materials Research at Stanford University and
because of availability of large items of research apparatus furnished
by the same source. With the onset of the NASA grant, work on CuBr,
CuI, CuCl, the alkali halides, CdSe, CdTe, and other II-VI compounds was
placed under it. These materials were chosen since they are either
presently being used in NASA programs as practical ultraviolet photo-
cathode materials or because they show promise of being useful as uv
photocathodes in the future. The prime object of the work is to use
photoemission and optical studies to determine the electronic band structure
of the materials. In order to do this, it is absolutely necessary to
determine fundamentals of the photoemission and, because of the details
of the experiments, that the effects of various vacuum conditions on the
photoemission from the materials be understood. In this process, it
should be possible to define the photoemission characteristics of these
materials much more precisely than has been possible in the past and to
make suggestions as to the ways in which optimum uv photocathodes may be
engineered.

In this report we shall cover fairly completely the work on CdSe, including a description of experimental difficulties encountered with the vacuum monochromator and the modifications used to overcome these. It is anticipated that the CdSe studies will be completed and an article written for publication within the next few months. Preprints will be made available at that time.

Representative data from CuI, CuBr, and CuCl are included in this report. A comprehensive report of this work will either be included in the next semi-annual report or be issued as a separate report before the next semi-annual report is available.

Some information on instrumentation and techniques are included here. When it seems appropriate, separate reports will be issued on these subjects.

Since the principal motivation of this work is the study of the fundamentals of the electronic structure and photoemission from these materials, certain aspects of the work which are of immediate interest to the users of practical uv photoemitters may not be strongly emphasized in sections where the emphasis is on reporting the basic work. To prevent the lost of information which may be of practical use, a section will be included at the end of this report entitled "Possible Implications for Practical Photocathodes."

II. WORK ON CdSe

A. Introduction

The research reported here is part of a systematic study of the photoemission from II-VI compounds. We are using photoemission techniques

in order to determine the energy band structure of these materials.
Although our primary goal is the experimental determination of the band
structure, additional results include information concerning the funda-
mental processes by which light is absorbed and processes in which elec-
trons lose energy through scattering; thus they have strong implications
for practical photoemission applications. We present in this report the
results of photoemission experiments performed on CdSe.

B. Experimental Techniques

The photoemission experiments have been performed on cleaved single
crystals of hexagonal CdSe obtained from Clevite Corp. and SemiElements.
Experiments have been performed under various ambient pressures ranging
from 10^{-4} torr to 10^{-9} torr. All experiments utilized an ultra high
vacuum chamber described by Kindig and Spicer.[1] A McPherson Model 225
vacuum monochromator was used. A sodium salicylate film was used as a
standard for measuring relative light intensity assuming that the yield
of the film is constant[2] for photon energies between 6 and 12 eV. The
absolute yield was measured with a Cs_3Sb photo tube calibrated by W. E.
Spicer.

It seems appropriate to mention here some of the difficulties which
we have overcome in the course of this research. By far the greatest
difficulty was a gradual decrease in intensity of light from our vacuum
monochromator over a period of several months. The Bausch and Lomb
grating was being covered with a film of contamination, the source of
which was traced to the hydrogen discharge lamp. This was verified by
inserting a glass disk near the discharge but between the discharge and
the grating. After running the lamp for about 3 hours, we removed the
glass and found a film of contamination on the side of the disk nearest
the lamp.

Once, believing that we had solved this problem, we inserted a new grating into the vacuum system. Three hours later the light intensity from the grating had fallen to 0.1 percent of its former value. We removed the grating and immediately rinsed it with xylene. This succeeded in completely restoring the grating to its initial condition. This is not always possible. The grating used prior to isolating the problem was contaminated about ten times over a period of several months. Each time a xylene rinse improved the condition of the grating somewhat, but gradually the intensity decreased to about 0.5 percent of that for a new grating.

We have now succeeded in eliminating this difficulty through the following corrective measures:

1. We use only ultra high purity gases in the lamp and continuously cold trap the gas line with liquid nitrogen.

2. All rubber tubing in the gas input line was replaced by copper tubing and the gas control valves were placed at the arc input so that the gas line can be kept at atmospheric pressure.

3. Viton O-rings are used for all vacuum seals in the lamp. Although the vacuum manufacturer's specifications called for neophreme O rings, we found that sufficient heat was produced in the arc to decompose these.

4. We apply an absolute minimum of vacuum grease to the O rings seals, particularly those nearest the discharge. Excess grease melts, flows into the discharge and is vaporized.

C. Experimental Results

We present in Fig. 1 the spectral distribution of the quantum yield for two samples of CdSe. The sample cleaved in low vacuum was exposed to 10^{-4} torr of hydrogen; the other sample was cleaved in a vacuum of approximately 10^{-9} torr. The effect of the presence of gas is striking.

It produced 1) a lowering of the electron affinity by about one volt relative to that for the sample cleaved in the 10^{-9} torr vacuum, and 2) a rise in yield for $h\nu \gtrsim 9$ eV which reaches a final value about four times as large as the highest yield for the sample cleaved in high vacuum. Later, using energy distribution data, we show that this is explained by the escape of secondary electrons produced by electron-electron scattering of the primary photoelectrons.

In Figs. 2 through 5 we present energy distributions of the photo-emitted electrons for the sample cleaved at 10^{-4} torr. In Figs. 6 and 7, energy distributions obtained from the sample cleaved in high vacuum are presented. The zero of electron energy in these curves is taken to be the top of the valence band. Except for $h\nu = 21.2$ eV, all energy distributions have been normalized to the quantum yield. The area under a given energy distribution is proportional to the quantum yield at that photon energy. The advantage of presenting the data in this manner is that after the normalization the vertical scale of an energy distribution is calibrated in electrons per incident photon per electron volt. Hence we may compare the number of electrons excited to a given final state for various photon energies. The data presented here is plotted in units of 10^{-2} electron per photon per electron volt.

Most of the structure in the energy distribution data can be understood in terms of features of the conduction and valence band structure and the matrix elements connecting this structure. For example, for a photon energy of 7.4 eV there is a strong transition from initial states near -1.6 eV to final states near 5.8 eV producing the peak at 5.8 eV in Fig. 2. We indicate with a dagger labeled CB1 the conduction band density of states peak located near 5.8 eV by means of these measurements.

For $h\nu = 8.8$ eV there is a strong transition from initial states near -1.6 eV to final states near 7.2 eV. We indicate with a dagger labeled CB2 the peak of electrons due to final states near 7.2 eV. This transition can be seen in both the samples (Figs. 2, 3, and 6). For other values of photon energy the peak of electrons due to initial states near -1.6 eV is indicated by an arrow labeled VB. The energy of this peak, as a function of photon energy, is given by

$$E = h\nu - 1.6 \text{ eV} \quad . \tag{1}$$

For photon energies between 7.4 and 10.6 eV there is a small peak of electrons whose position in energy is given by

$$E = 0.4 \, h\nu + 2.7 \text{ eV} \quad . \tag{2}$$

The location of this peak is indicated by the arrow labeled DT. For $h\nu = 7.4$ eV this peak is due to transitions from valence band states at -1.6 eV to the conduction band states mentioned previously at 5.8 eV. For $h\nu = 10.6$ eV this peak is located at $E = 7.2$ eV, the same energy as the conduction band high density of states. The peak is not seen for photon energies greater than 10.6 eV. The disappearance of this peak may be the result of selection rules or the peak may be masked by the large number of slow electrons observed in the energy distributions for photon energies greater than 10.0 eV. In either case, the fact that the peak's location changes by amounts less than the increments in photon energy is indicative of direct transitions.[3]

In Fig. 3 we find additional evidence of the presence of direct transitions. For $h\nu = 8.8$ eV the peak of electrons VB coincides with the peak of electrons CB2 since the states near -1.6 eV are coupled to final

states near 7.2 eV. For higher photon energies the peak VB moves in accordance with Eq. (1). But the peak of electrons CB2 disappears from the energy distribution for photon energies greater than about 9.6 eV. If the photoemission were determined solely by the valence band and conduction band densities of states, then one would expect[4] the amplitude of the peak CB2 to be modulated by the valence band density of states at $7.2 - h\nu$ eV, but not to disappear entirely. Hence we conclude that for $h\nu = 8.8$ eV a large fraction of the electrons near CB2 results from direct transitions.

For photon energies greater than about 10.0 eV a large peak of slow electrons appears in the energy distributions. As previously notes, the quantum yield also begins to rise for $h\nu \geq 10$ eV for the low vacuum cleaved sample. We believe that this rise is due to the escape of both primary and secondary electrons when the primary photoelectrons are inelastically scattered. From the energy distributions it is apparent that it is possible for an electron to escape the semiconductor if it has an energy greater than about 5 eV. Hence it is possible to have a scattering event in which both primary and secondary electrons escape the semiconductor when the primary electron has an energy greater than 10 eV. Since the primary electrons are photogenerated, we expect these events to occur when the photon energy is greater than about 10 eV.

In Fig. 5 we present the energy distribution of the photoemitted electrons for $h\nu = 21.2$ eV. Many of the photoelectrons have been electron-electron scattered to states near the peak in the conduction band density of states CB1. The peak of electrons labeled D at an energy of 11.4 eV is believed to be due to transitions from a high density of states at -9.8 eV in the valence band. It is possible that these states arise from the 4d electrons on the cadmium ions.

In Fig.s 6 and 7 we note that the electron affinity is approximately
a volt larger for the high vacuum cleaved sample than for the low
vacuum cleaved sample. Consequently, the strong transition for hν =
7.4 eV is not observed here since the final state now lies in the
threshold region. As discussed above, the peak indicated by an arrow
VB is due to excitation from a high density of states 1.6 eV below the
top of the valence band. For a photon energy of 8.8 eV, this high
density of states in the valence band is coupled with final states at
7.2 eV in the conduction band. The peak of electrons due to these
states in the conduction band is indicated by a dagger CB2. For photon
energies greater than 10.2 eV there is a shoulder in the energy distri-
butions labeled S at an energy of about 0.5 eV below the highest energy
electron. It appears that this shoulder is due to structure in the
conduction band density of states. Note that the loss of high energy
electrons due to inelastic scattering is definitely less in these
samples than in those cleaved in the poorer vacuum.

IV. RELATION OF PHOTOEMISSION TO BAND STRUCTURE AND REFLECTIVITY

We have established the presence of direct as well as nondirect
transitions in the photoemission of CdSe. Furthermore, since the peak
of electrons VB follows Eq. (2) over such a large energy range, it is
apparent that these electrons result from nondirect transitions[4] at most
photon energies, although the strong peak in the 8.8 eV energy distri-
bution clearly has a strong direct component. The same may be true
for the 7.4 eV peak.

We feel that the photoemission data are consistent with the band structure shown in Fig. 8. CB1 is associated with the conduction band states Γ_5, Γ_1 in energy, and CB2 is assigned to conduction band states near Γ_6 in the conduction band. For $h\nu = 8.8$ eV we observe direct transitions from states near Γ_6 in the valence band to states near Γ_6 in the conduction band. For $h\nu = 7.4$ eV the states near Γ_6 in the valence band are coupled to states near Γ_5, Γ_1 in the conduction band. Although we have demonstrated that the peak DT is evidence of direct transitions, at this time we are not able to specify the location in the Brillouin Zone of the initial and final states for $h\nu > 7.4$ eV. For $h\nu = 7.4$ eV the initial states are near Γ_6 and the final states are near Γ_5, Γ_1.

The ultraviolet reflectivity of CdSe measured by Cardona is shown in Fig. 9. We assign the E_1' peak in the reflectivity for $h\nu = 8.6$ eV to transitions from states in the vicinity of Γ_6 in the conduction band. This is in agreement with the interpretations of Phillips[5] and Cardona.[6] On the basis of the photoemission data we assign the E_2 peak in the reflectivity for $h\nu = 7.5$ eV to transitions from states in the vicinity of Γ_6 in the valence band to final states in the vicinity of Γ_5 in the conduction band. This peak in the reflectivity has not previously been assigned to any region of the wurtzite Brillouin zone.

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3. C. N. Berglund and W. E. Spicer, Phys. Rev. $\underline{136}$, A1030 (1964); Phys. Rev. $\underline{136}$, A1044 (1964).

4. Reference 3 and C. N. Berglund, Proc. Intern. Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, to be published; W. E. Spicer, Proc. Intern. Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, to be published.

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Fig. 1   Spectral distribution of the quantum yield from CdSe.

Fig. 2   Energy distributions for sample cleaved at 10^{-4} torr; $h\nu = 6.8, 7.4, 8.0, 8.4, 8.8$ eV.

Fig. 3   Energy distributions for sample cleaved at 10^{-4} torr; $h\nu = 8.8, 9.6, 10.0$ eV.

Fig. 4   Energy distributions for sample cleaved at 10^{-4} torr; $h\nu = 10.0, 10.4, 11.0, 11.6$ eV.

Fig. 5   Energy distributions for sample cleaved at 10^{-4} torr; $h\nu = 21.2$ eV.

Fig. 6   Energy distributions for sample cleaved in a vacuum of 10^{-9} torr; $h\nu = 7.8, 8.2, 8.8, 9.4, 9.8$ eV.

Fig. 7   Energy distributions for sample cleaved in a vacuum of 10^{-9} torr; $h\nu = 9.8, 10.2, 10.6, 11.2, 11.6$ eV.

Fig. 8   Energy band structure of CdSe as inferred from photoemission studies.

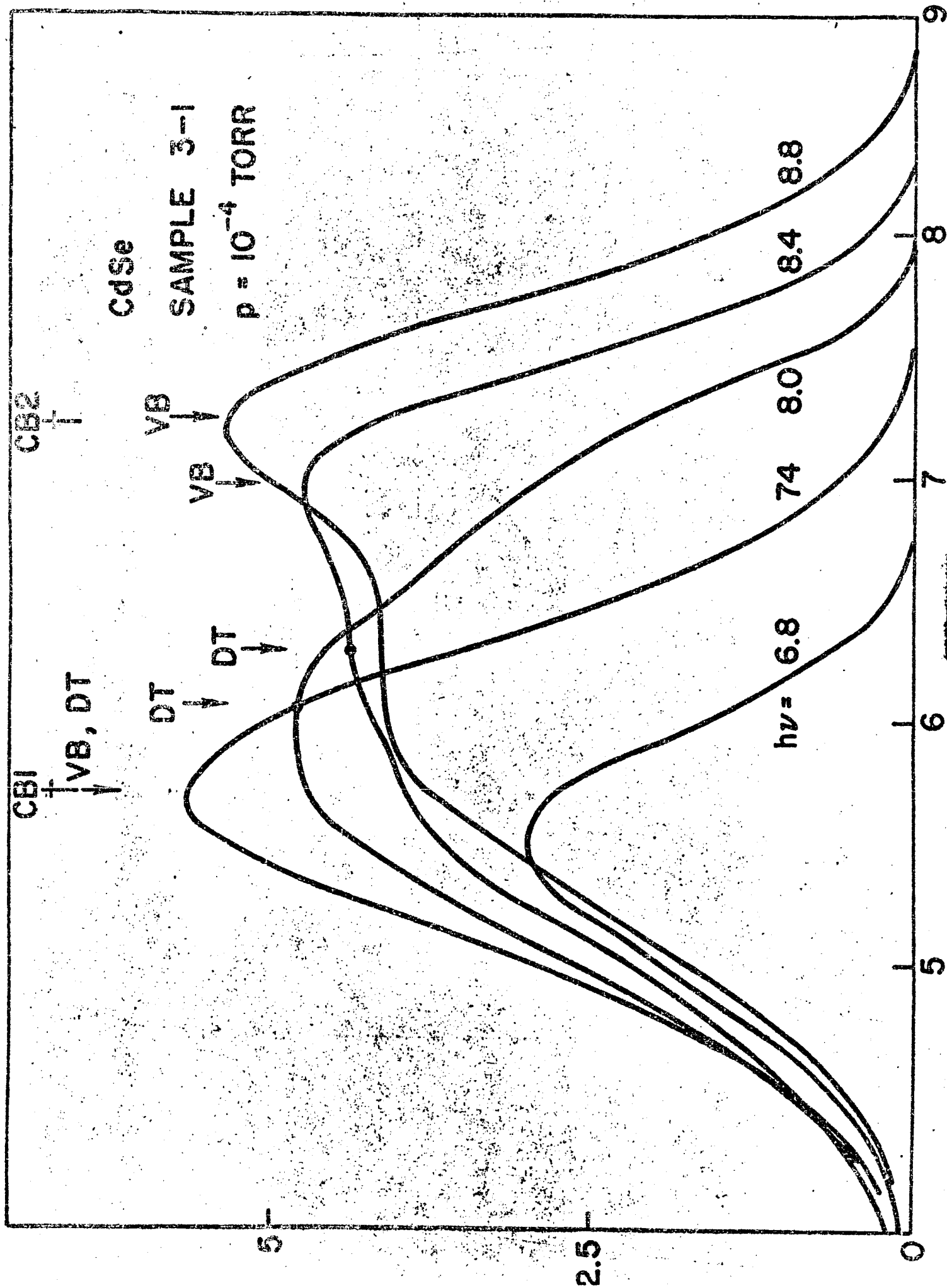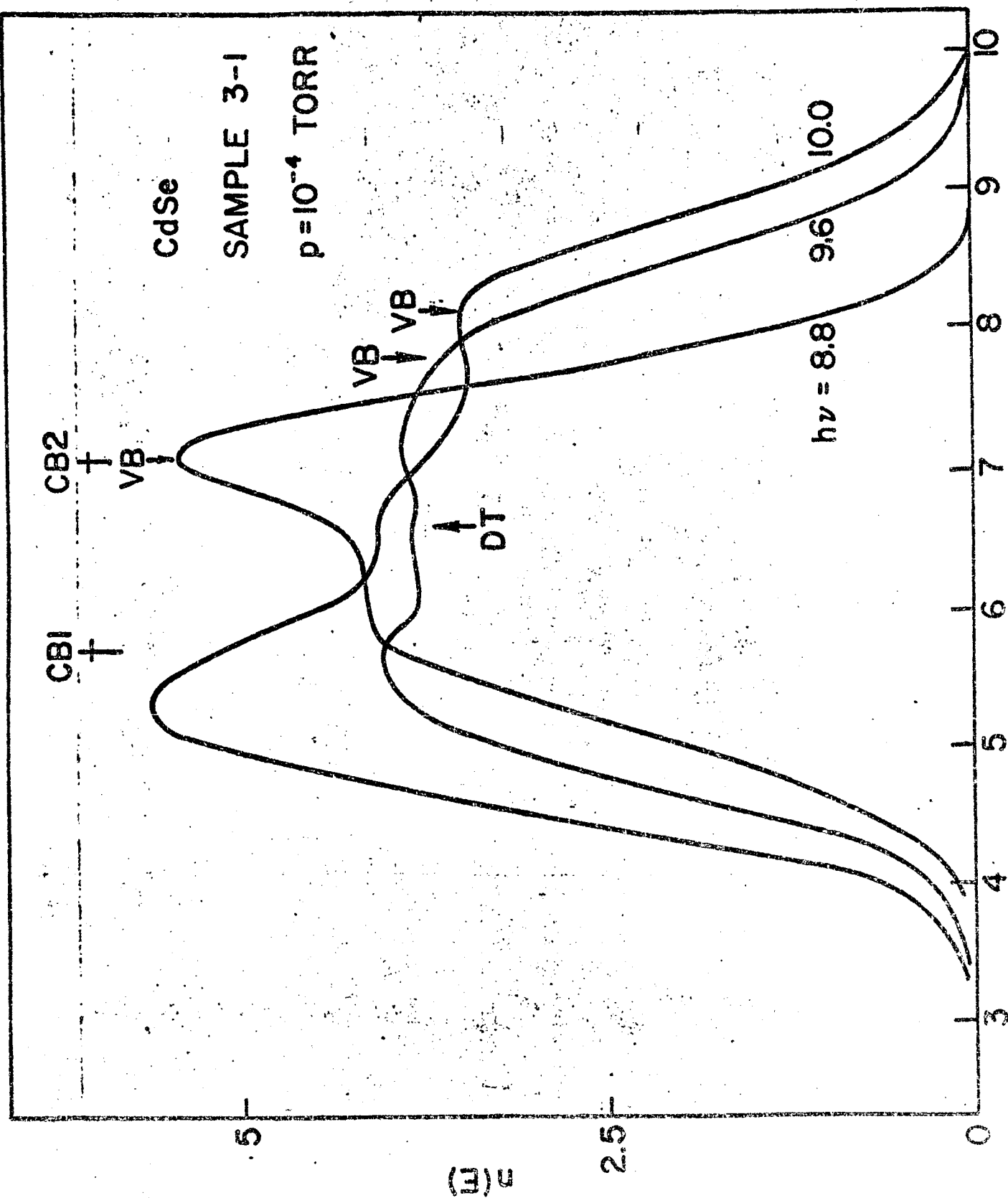Fig. 9   Reflectance of CdSe measured by Cardona (Ref. 7).
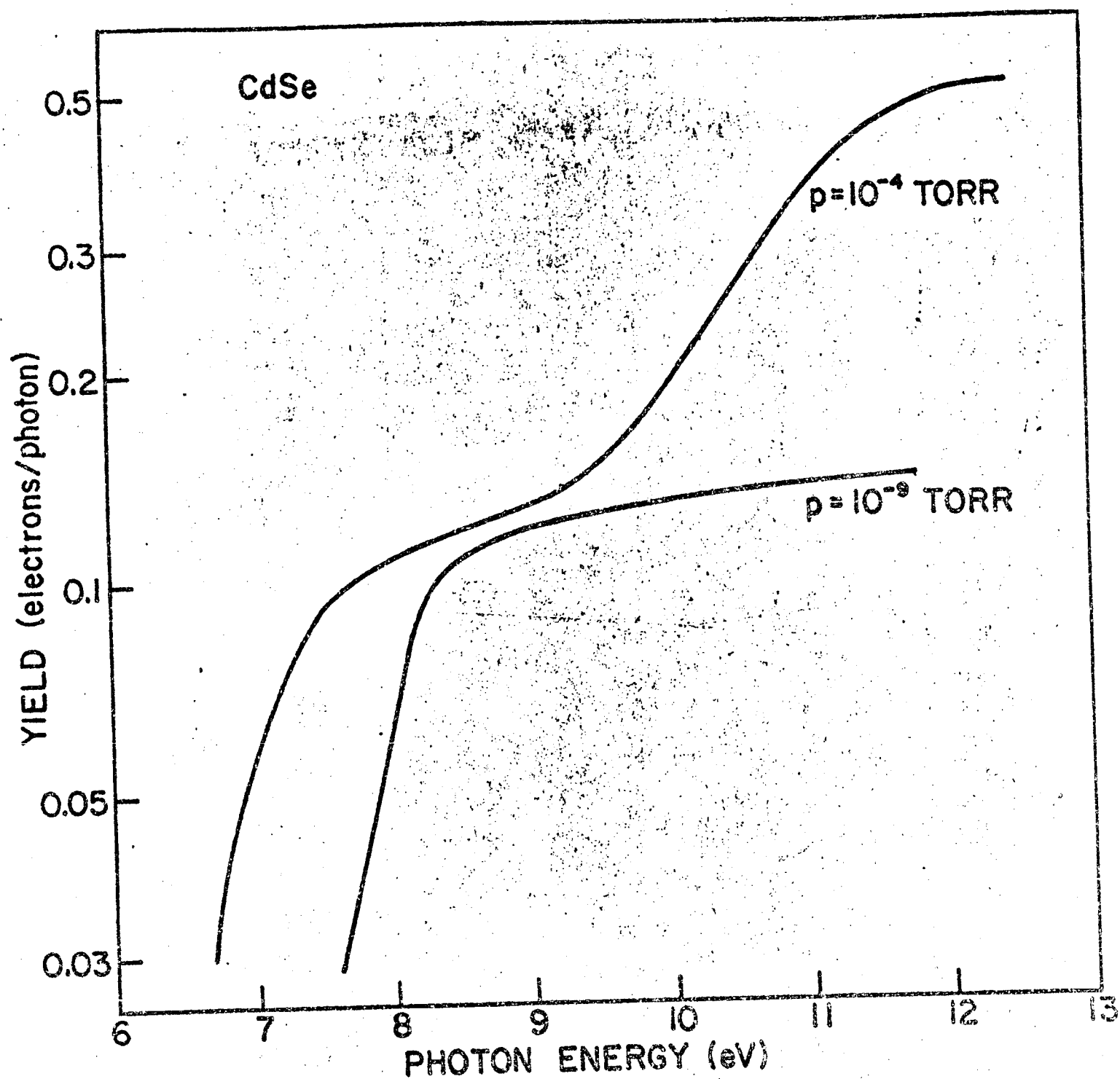
Fig. 1
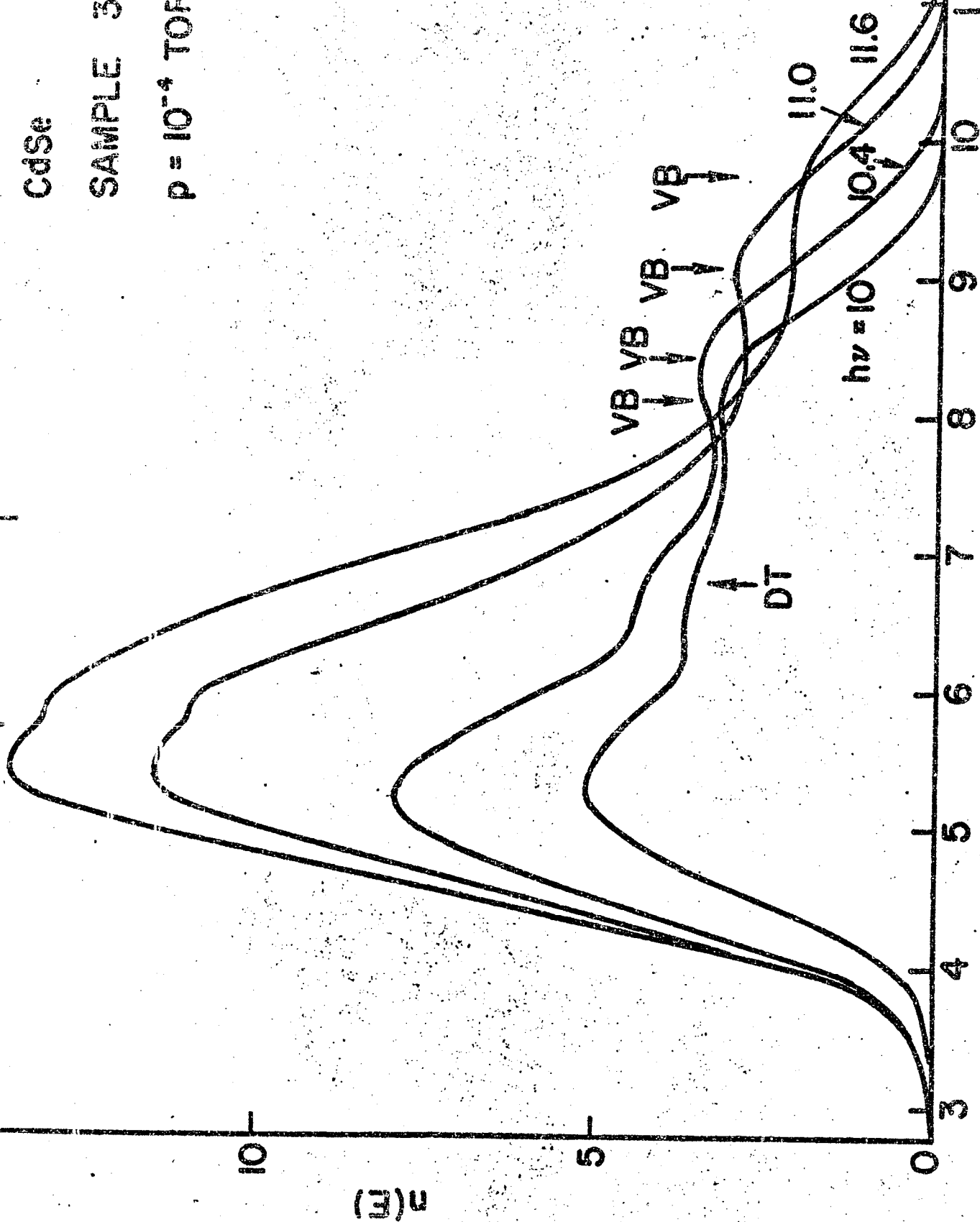
A-35057

CdSe
SAMPLE 3-1
$p = 10^{-4}$ TORR

Fig. 2

Fig. 3

CdSe
SAMPLE 3-1
p=10⁻⁴ TORR

A-35060

CdSe
SAMPLE 3-1
p = 10⁻⁴ TORR

Fig. 4

CdSe
SAMPLE 3-1
p = 10⁻⁴ TORR

hν=21.2

x5

D

CB2

CBI

CdSe
SAMPLE 3-3
p = 10⁻⁹ TORR

CdSe
SAMPLE 3-3
$p = 10^{-9}$ TORR

CB2

VB VB
VB
VB
VB
VB

S
S
S

$\hbar\omega = 9.8$ 10.2 10.6 11.2 11.6

$\eta(E)$

7.5

5

2.5

0

7 8 9 10 11

Fig. 7

Fig. 8

A-35059

Cd Se

— CARDONA

5.1

7.6

8.7

9.5

6.1

REFLECTIVITY (percent)

50

40

30

20

PHOTON ENERGY (ev)

4   5   6   7   8   9   10
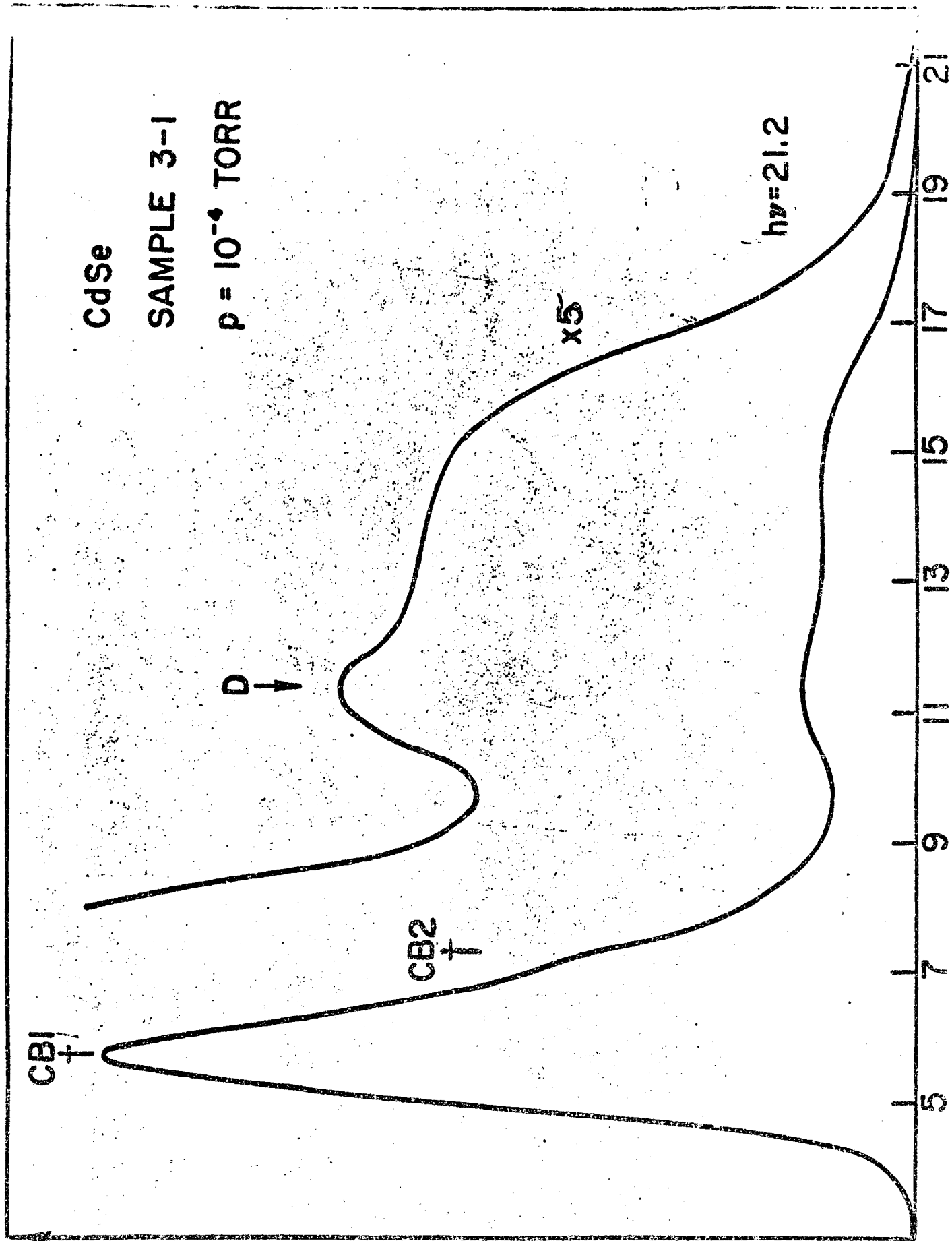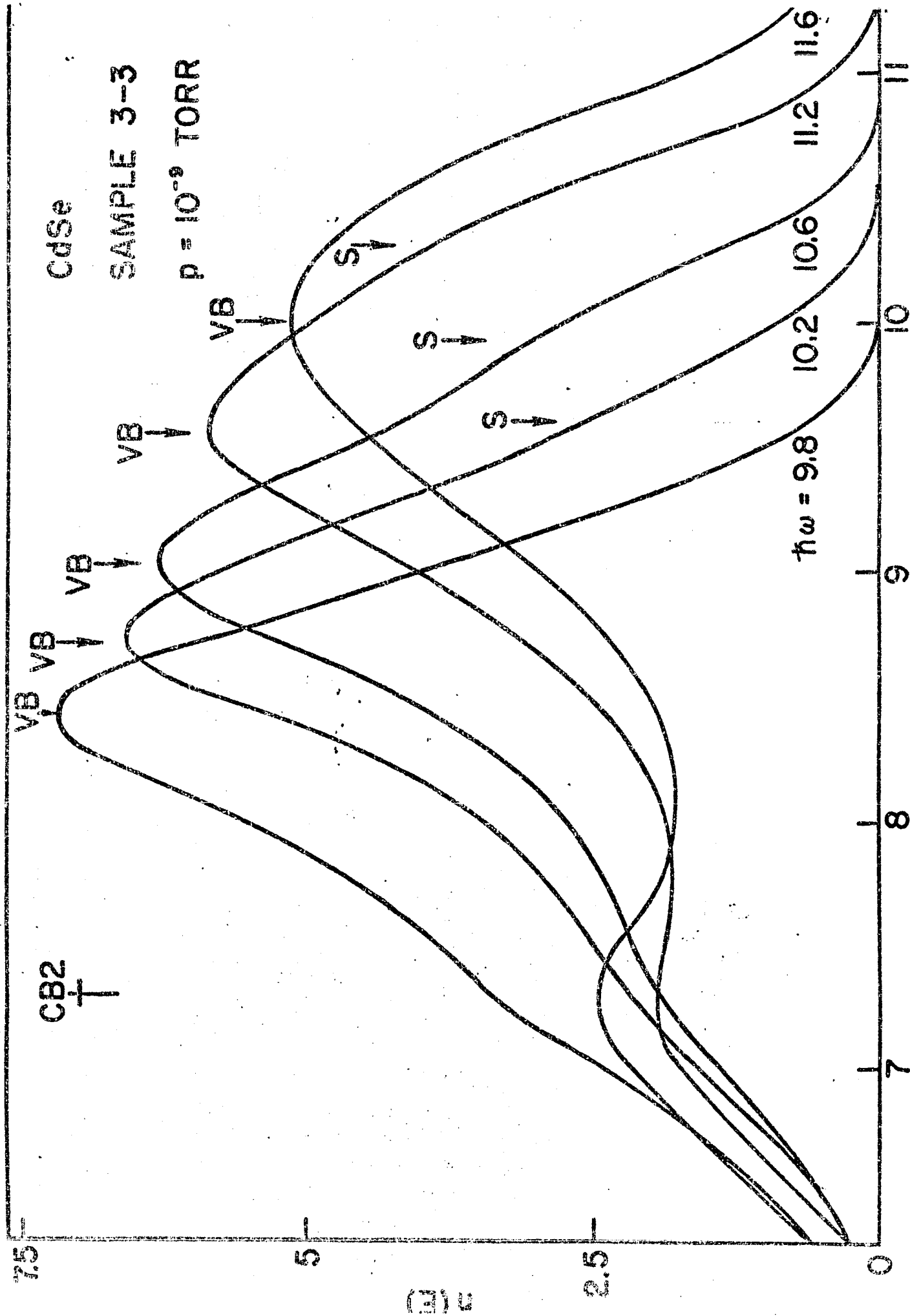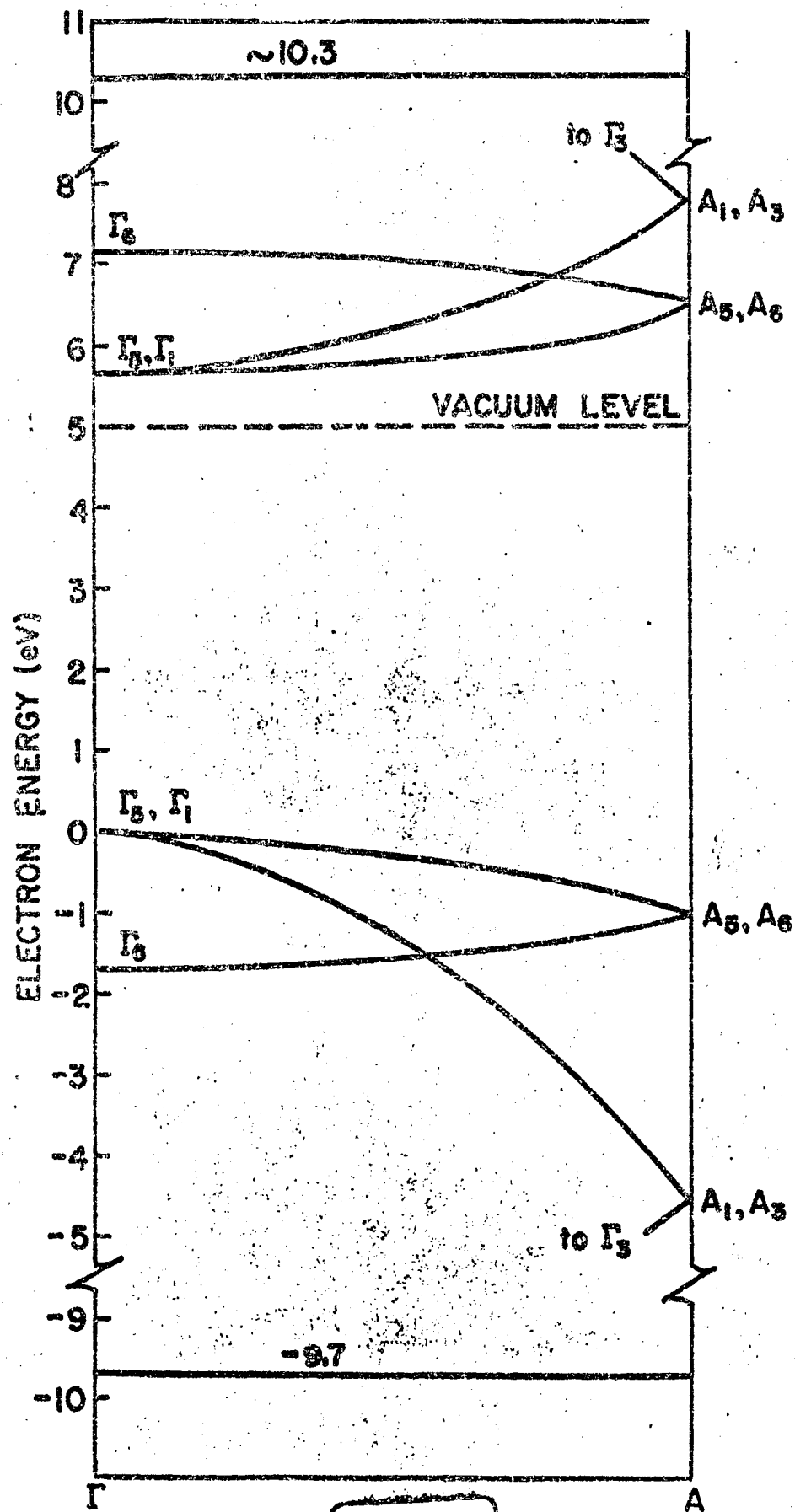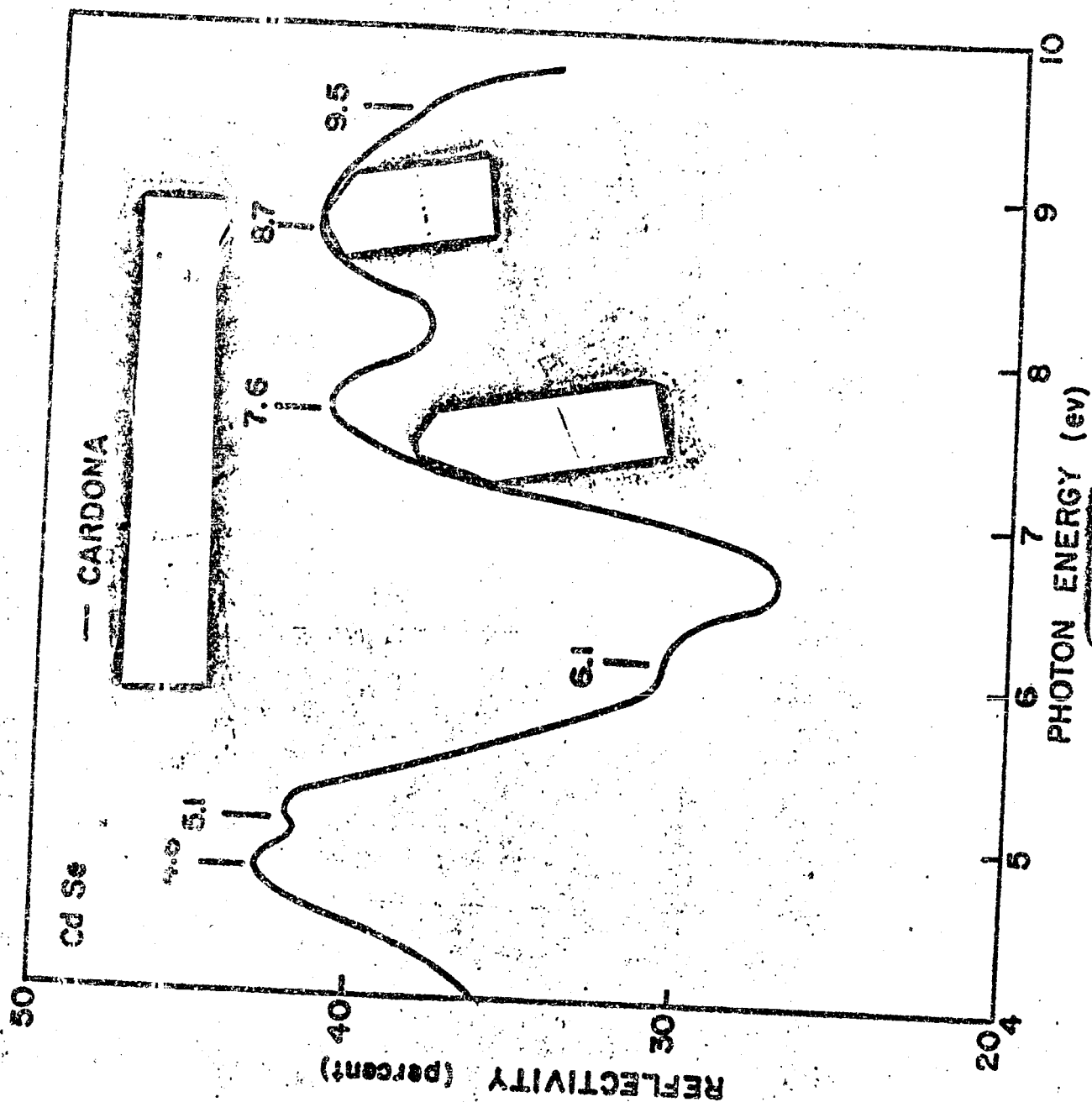
Fig. 9

III. WORK ON CuI, CuBr, AND CuCl

Photoemission measurements have been made on CuI, CuBr, and CuCl samples formed by evaporation under a good vacuum (p $\gtrsim$ 10^{-8} Torr) and on one sample prepared under less ideal vacuum conditions. The Cu halides were purified by vacuum distillation before being placed in the experimental tube or chamber. The spectral distribution of quantum yield and the energy distribution waves were taken in the spectral range between the threshold for emission (hv > 5 eV) and the cutoff of the LiF window (approximately 11.8 eV). Representative quantum yield curves are given in Fig. 10 for the samples prepared in good vacuum conditions.

A comprehensive report on these studies giving much more complete energy distribution data will be prepared at a later date. Curves giving the results from CuI at hv = 9.4, 10, and 11.8 eV are given in Figs. 11, 12, and 13 as examples of the results obtained in this work. In Fig. 14, data are presented for a CuCl sample which was subjected to poorer vacuum conditions (Curve 1) than that for the samples described above (Curve 2 in Fig. 14).

Using the results of the photoemission and optical studies, the important features of the band structure and optical selection rules are being deduced for the cuprous halides. Very high valence densities of states are found at energies approximately 4 eV less than the valence band maximum. This provides the strong peak seen at E = 0.55 eV in Fig. 12 as well as the peaks at 1.95 and 1.18 eV in Fig. 13. There are at least two peaks in the density of states lying between this structure and the top of the valence band. Both direct and nondirect transitions are observed from this band. The structure in Fig. 11 for E > 0.6 eV and in

Fig. 12 for $E > 1.35$ eV is due to transition from these states. The electrons with $E > 3.1$ eV in Fig 13 are also due to excitation from these states. It appears quite likely that the high densities of states located at 4.0 eV or more below the valence band maximum are derived principally from the Cu d-bands. Further work is being done to find the origin of the states within 4 eV of the valence band edge. As part of this investigation, studies will be made of the alkali-halides.

The data presented in Fig. 14 gives one example of the effect of poorer vacuum conditions on the photoemission from the cuprous halides. Curve 1 was taken from a tube designed so that the window could be removed after the CuCl photocathode had been formed in a relatively good vacuum. This was done so that the window could be removed in the vacuum, allowing measurement to be made at wavelengths below 1050 Å (the cutoff of a LiF window).
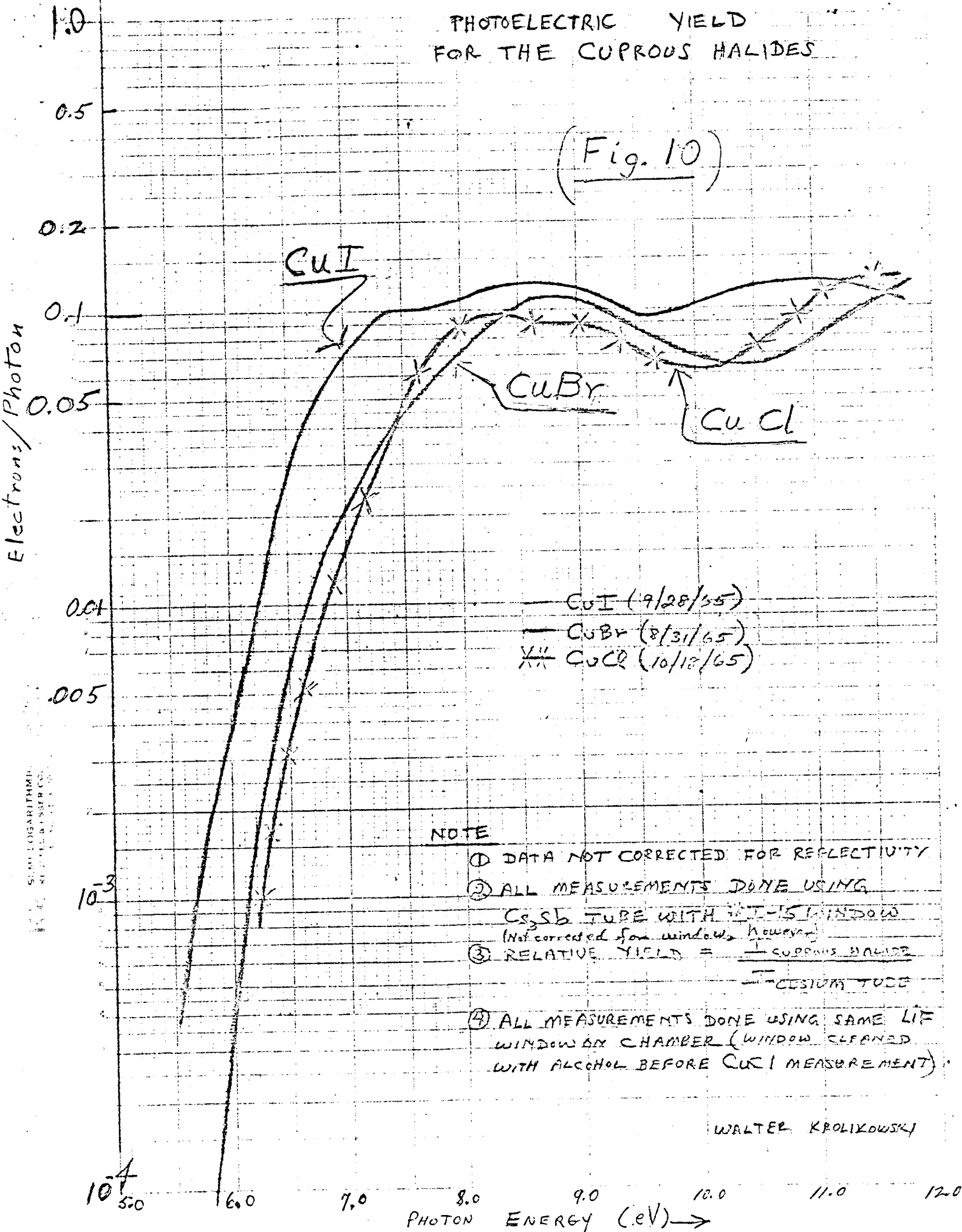
In this way Curve 2 in Fig. 14 has been extended to 910 Å (13.6 eV). The window was attached to the tube using a neophrene "O" ring. In the outgassing process, it was noticed that some decomposition of the "O" ring took place producing a colorless liquid. After the photocathode was evaporated and the tube was sealed off, it was placed in the vacuum monochromator and the window was removed after a vacuum was obtained in the monochromator. As can be seen in Fig. 14, marked changes were produced in the yield curves by the poorer vacuum. Unfortunately, it is impossible to say what part of the differences between Curves 1 and 2 is due to the poorer vacuum conditions under which the cathode of 1 was formed and what part is due to the effects of the higher pressure ($\sim 10^{-3}$ Torr--principally H_2) to which surface 1 was exposed during measurements.

We are now building tubes which will remove this ambiguity. These are
high vacuum tubes using normal AgCl seals for the LiF windows. The
windows are mounted on thin glass arms so that they can be sheared off
in the vacuum monochromator. With these tubes we will make measurements
under good vacuum, then shear off the window and make measurements
including those for $h\nu > 11.8$ eV.

Fig. 10   The spectral distribution of quantum yield for CuI, CuBr, and CuCl sample prepared under good vacuum condutions (pressure $\leq 10^{-8}$ torr).

Fig. 11   The distribution in energy of the electrons emitter from CuCl prepared in good vacuum for $h\nu = 9.4$ eV. The relative number of electrons emitted per eV is plotted on the abscissa. The energy of the emitted electrons is plotted on the ordinate.

Fig. 12   Energy distribution from CuCl for $h\nu = 10$ eV.

Fig. 13   Energy distribution from CuCl for $h\nu = 11.8$ eV.

Fig. 14   Spectral distribution of quantum yield for CuCl sample prepared in good vacuum, pressure $\leq 10^{-8}$ torr, curve (1); and in poor vacuum, curve (2).

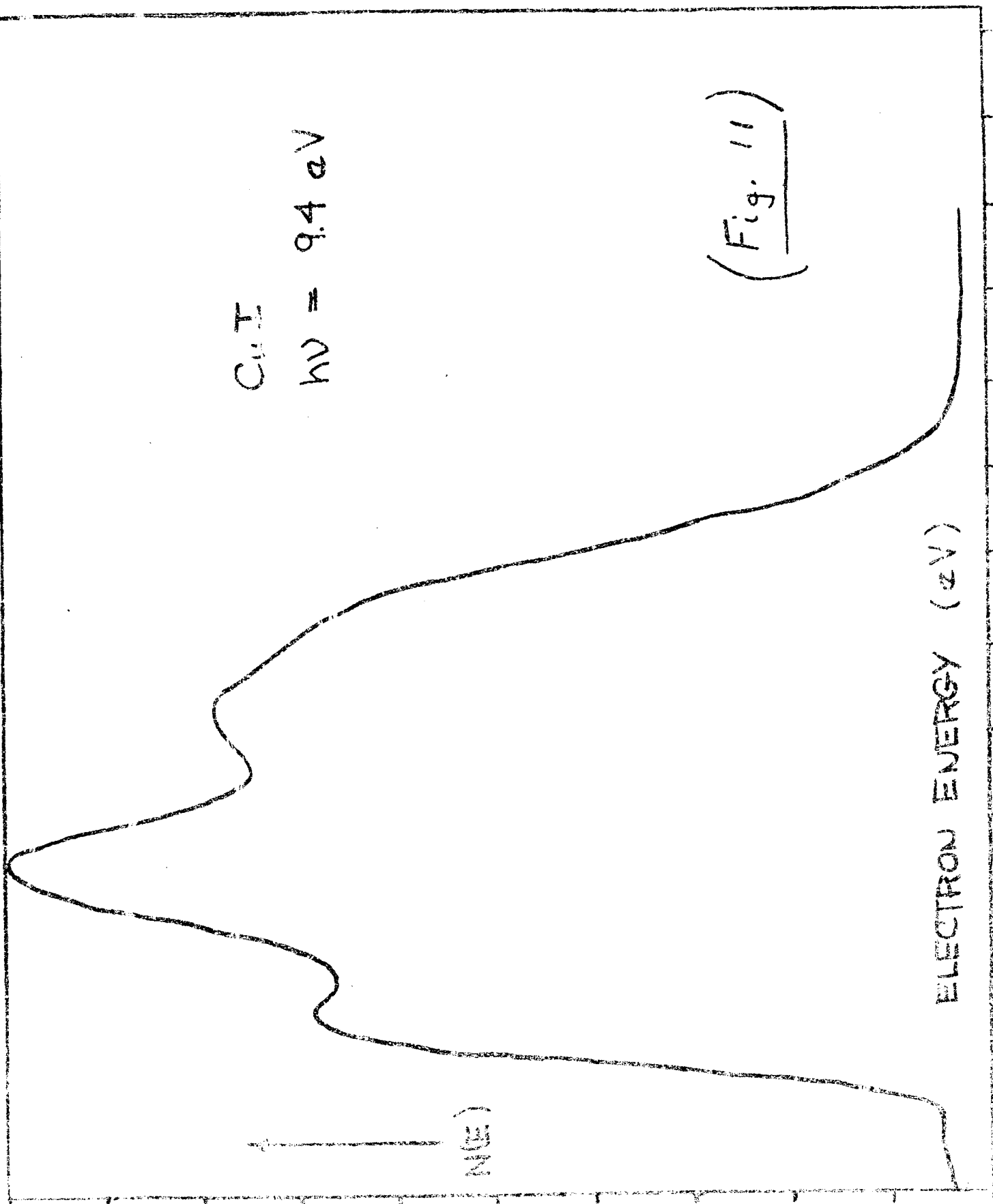PHOTOELECTRIC YIELD FOR THE CUPROUS HALIDES

(Fig. 10)

CuI

CuBr

Cu Cl

Electrons/Photon

—— CuI (9/28/55)
—— CuBr (8/31/65)
XX CuCl (10/18/65)

NOTE

① DATA *NOT* CORRECTED FOR REFLECTIVITY

② ALL MEASUREMENTS DONE USING
Cs_3Sb TUBE WITH LiF-15 WINDOW
(Not corrected for window, however)

③ RELATIVE YIELD = $\frac{I \ \text{CUPROUS HALIDE}}{I \ \text{CESIUM TUBE}}$

④ ALL MEASUREMENTS DONE USING SAME LiF
WINDOW ON CHAMBER (WINDOW CLEANED
WITH ALCOHOL BEFORE CuI MEASUREMENT)

WALTER KROLIKOWSKI

PHOTON ENERGY (eV) →

Cu I
$h\nu = 9.4\ eV$

N(E)

ELECTRON ENERGY (eV)

(Fig. 11)

Cu I
hν = 10.0 eV

(Fig. 12)

N(E)
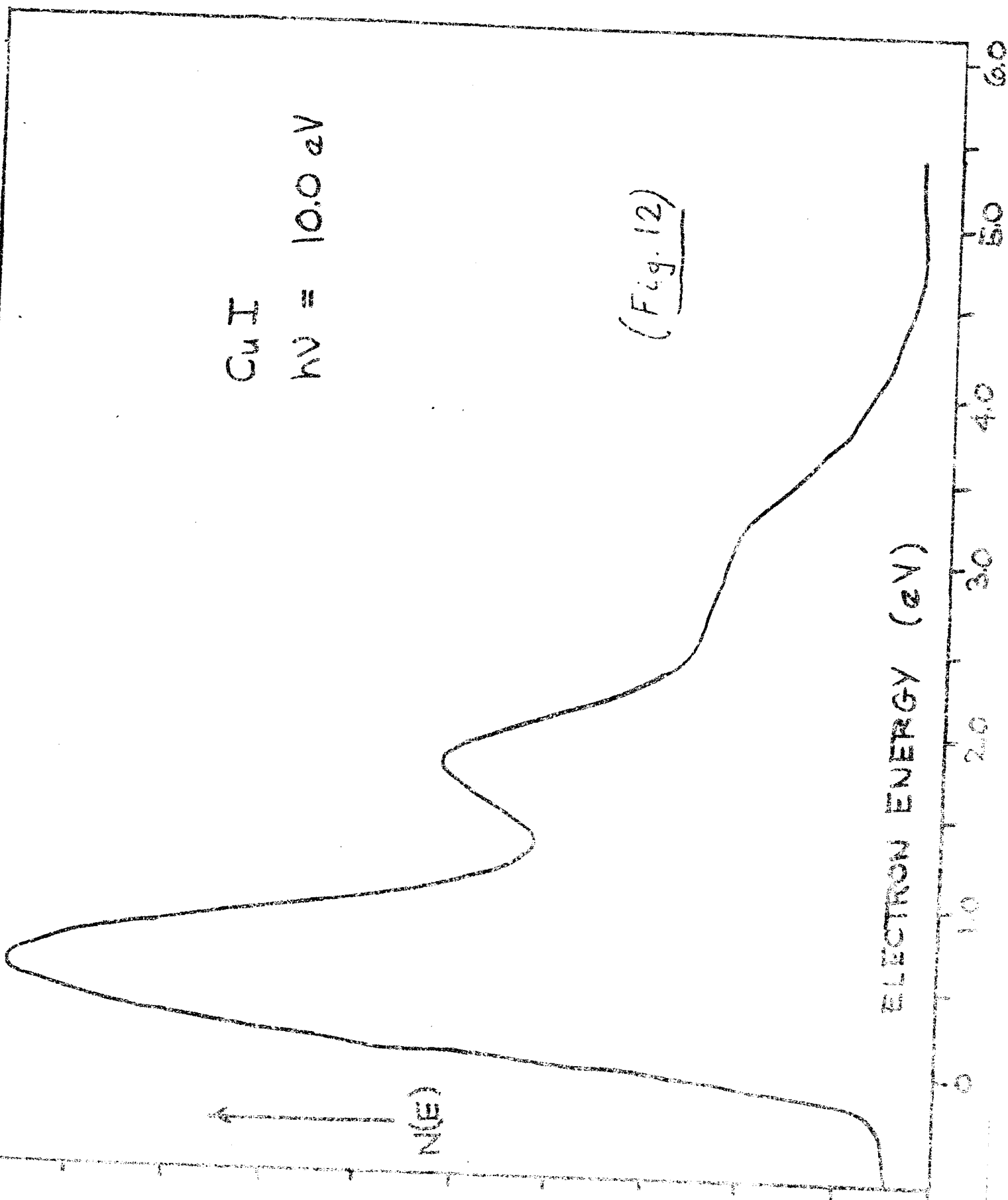
ELECTRON ENERGY (eV)

CuI

$h\nu = 11.8\ eV$

(Fig. 13)

ELECTRON ENERGY (eV)

N(E)

(Fig. 14)

CuCl

① KNOCK OFF TUBE (NEOPRENE "O" RING)

② SEALED ULTRA-HIGH VACUUM TUBE

ABSOLUTE YIELD

PHOTON ENERGY [eV]
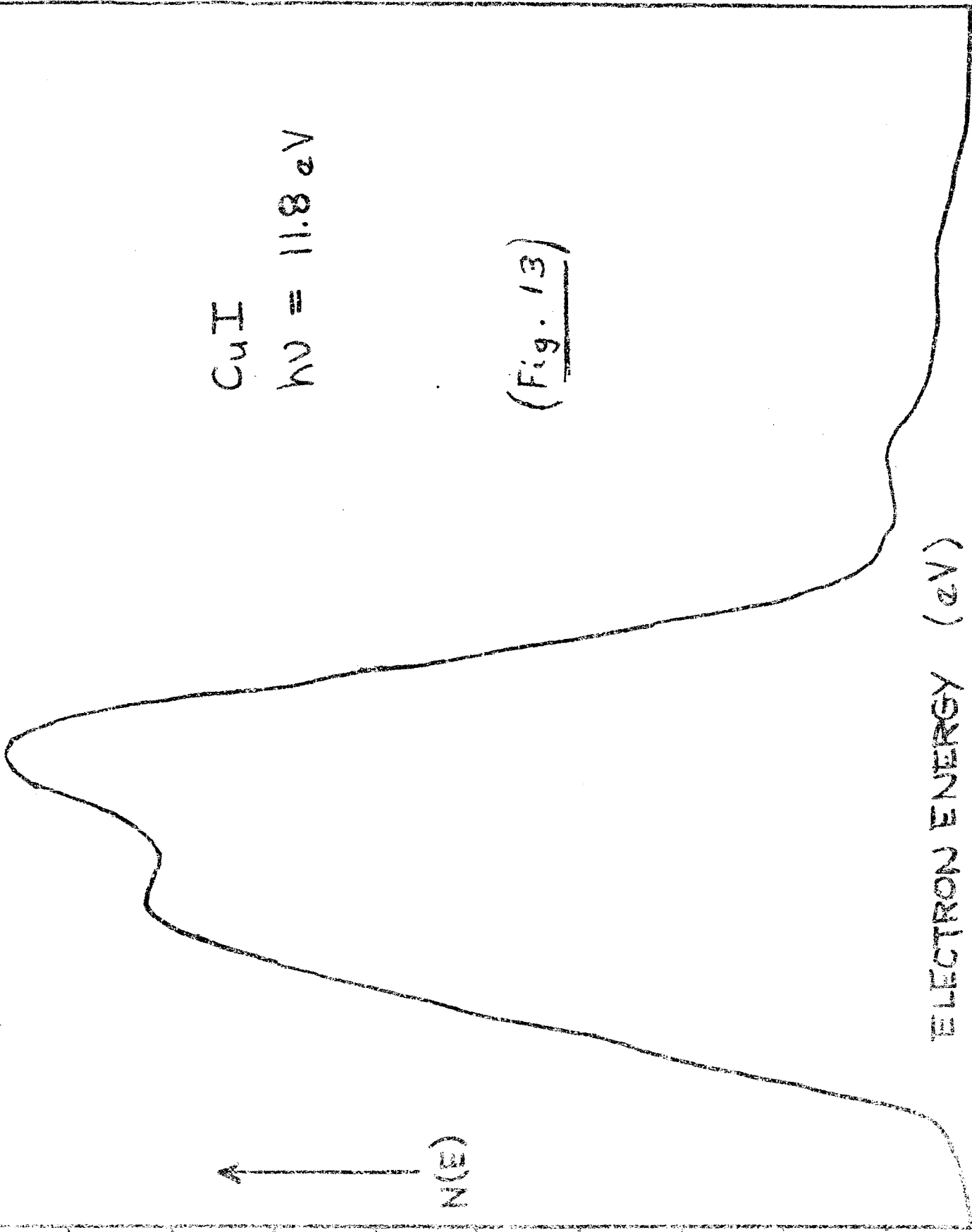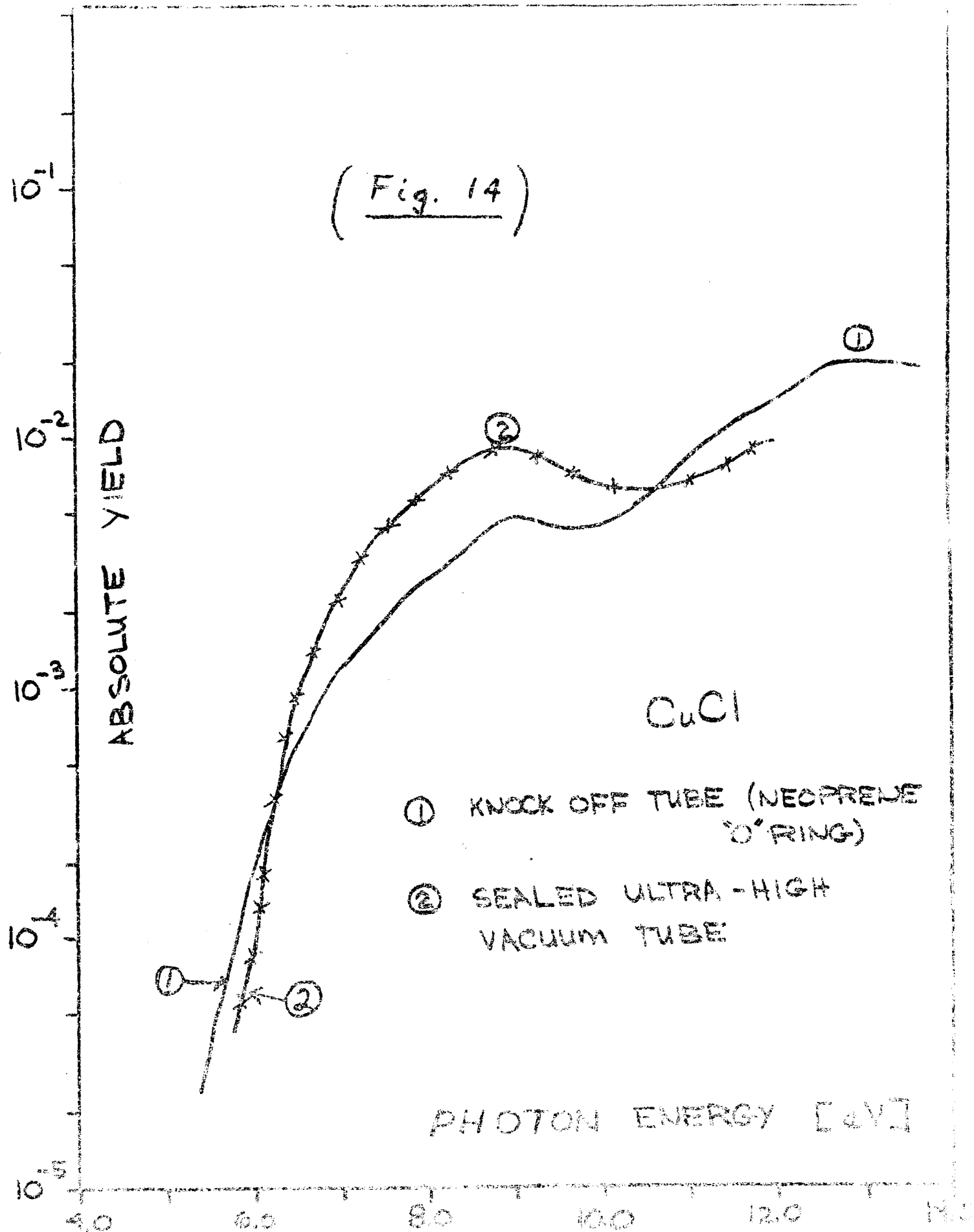
IV. POSSIBLE IMPLICATIONS FOR PRACTICAL uV PHOTOCATHODES

The effects of vacuum conditions on the photoemission found in these investigations are probably worthy of note. In studies of CdS[8,9] as well as the semiconductors reported here, it has been consistently found that exposure of a clean (cleaved) surface to foreign gases (usually O_2, H_2, or air) moves the photoemissive threshold toward longer wavelengths. In CdS sufficient data is available[8,9] so that a detailed comparison can be made. For this material, it appears that exposure to relatively low pressure of gas (for example the predominantly H_2 atmosphere of approximately 10^{-3} Torr of the vacuum monochromator) produces both the largest increase in yield and the largest movement of the threshold of response toward longer wavelength. In both CdSe (Fig. 1) and CdS the threshold was reduced by almost 1 eV (300 $\overset{o}{A}$) when the crystal was cleaved in the vacuum of the monochromator. For both materials the yield was also found to have increased at all wavelengths. The energy distribution curves gave evidence of increased energy loss due to scattering. The large gain in yield in the CdSe sample (Fig. 1) for $h\nu > 9.0$ eV seems to be due to the escape of the secondaries and primaries involved in the electron-electron (pair-production) scattering process.[6,10] It is also possible that the fact that the yield of the CuCl sample prepared poor vacuum (Curve 1 - Fig. 14) rises above the yield of the sample prepared under good vacuum conditions (Curve 2 - Fig. 14) for $h\nu > 10.5$ eV is due to the production and escape of secondaries.

Whereas, it appears that exposure to a small amount of gas (e.g., 10^{-3} Torr) may have a beneficial effect on the emission; it also appears

that exposure to a large amount of gas (e.g., atmospheric pressure) reduces the yield considerable although it may move the threshold toward longer wavelength. It also seems that exposure to gas reduces the sharpness of the long wavelength cutoff.

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V. PAPERS TO BE PRESENTED AT AMERICAN PHYSICAL SOCIETY MEETING IN LOS ANGELES DEC 20-22, 1965

1. J. L. Shay and W. E. Spicer, Photoemissive Investigation of the CdSe Band Structure.

2. W. F. Krolikowski and W. E. Spicer, **The Energy Band Structure of the Cuprous Halides.**